AD _____

CONFIDENTIAL

Progress Report No. M-54-1-ONR

IMPROVED LIQUID PROPELLANTS
Systems with Hydrazine
Hydrazine Derivatives

METALECTRO CORPORATION
Laurel, Maryland

March 1, 1954 Copy No. 1

CONFIDENTIAL

CONFIDENTIAL

METALECTRO CORPORATION

Contract: Nonr-163(01)
Subject: Hydrazine Derivatives

I M P R O V E D L I Q U I D P R O P E L L A N T S

Systems with Hydrazine

Hydrazine Derivatives

Written by: _____
D. Horvitz
Project Leader

Approved by: _____
H. Osborg
President &
General Manager

Date: March 1, 1954

CONFIDENTIAL

CONTRACT FULFILLMENT

This Progress Report is submitted in partial fulfillment of Contract Nonr-163(01) and includes investigations performed within the period January 1, 1953, to February 28, 1954. As indicated within the report, a considerable body of work, relating primarily to synthetic methods, is not included herein, but is being incorporated in a detailed Technical Report now in preparation.

I. INTRODUCTION

This informal progress report is being issued in order to bring to date the present status of work performed in conjunction with ONR Contract Nonr 163(01). Consistent with the purpose of an informal status report the work is presented in brief form. A detailed technical report is under preparation and will include a full account of all the work performed within the period covered.

As indicated in previous reports, the work on this contract includes the development of new products useful as rocket propellants, and the study and determination of their physical, chemical, and other characteristics. Investigations of preparative methods for these products required an evaluation of the known methods, which lead either to their modification or to the development of novel processes.

In line with this general program, further experiments concerned with the preparation and characterization of ethylenehydrazine have been performed; additional physical and chemical properties of methylhydrazine and unsymmetrical dimethylhydrazine have been determined; synthetic methods have been studied and developed.

A considerable amount of exploratory work has been performed in connection with the development of synthetic methods for the

methyl hydrazines and detailed data on these investigations will be incorporated in the technical report which is now being prepared. The need for development of synthetic methods, at least to a stage where questions concerning potential availability and cost can be answered with some degree of assurance, has become very evident during the course of the work. After earlier Metalectro reports had aroused a strong interest in the methyl hydrazines, it was found that the many inquiries which followed inevitably put first emphasis on availability and cost. Furthermore the request by ONR to furnish several hundred pounds of these materials in a very short period of time (6 months) with a relatively limited budget could not have been fulfilled to any appreciable degree by any method now available in the literature. That the distribution of these materials to the interested agencies was well worthwhile is amply demonstrated by the surge of response following the opportunity to make tests with these compounds.

II. SUMMARY

1. Viscosities and densities of methylhydrazine and unsdimethylhydrazine were determined over a wide range of temperatures. At -52°C (-61.6°F) the density of methylhydrazine is .433 gms/ml and its absolute viscosity is 13.319 centipoises.

At -55.0°C (-67.0°F) the density of uns-dimethylhydrazine is 0.8684 gms/ml and its absolute viscosity is 5.114.

2. Comparative tests of methylhydrazine, uns-dimethylhydrazine and hydrazine with various materials reveals that many substances which are able to catalyze violent decomposition of hydrazine or methylhydrazine in the presence of air have little or no effect on uns-dimethylhydrazine. For example, contact with the common insulating variety of asbestos caused spontaneous ignition of hydrazine at the end of 3 minutes and ignition of methylhydrazine at the end of 8 minutes, but when uns-dimethylhydrazine was contacted with this asbestos no ignition occurred and not even a temperature rise could be observed during a test period of 35 minutes.

3. Efforts were continued to develop improved methods for the preparation of ethylenehydrazine. A sample of pure ethylenehydrazine was prepared. It had a melting point of -40.5 °C.

4. Further progress was made in the effort to prepare N, N-dimethyl-N', N', -ethylenehydrazine, a method having been developed for the preparation of the intermediate, N-B-hydroxyethyl-N', N'-dimethylhydrazine.

5. A program to produce and to distribute several hundred pounds of methylhydrazine and uns-dimethylhydrazine to various

agencies was carried out successfully.

III. EXPERIMENTAL WORK

1. The Viscosities and Densities of Methylhydrazine and Uns-Dimethylhydrazine.

The viscosities and densities of highly purified samples of methylhydrazine and uns-dimethylhydrazine were determined over a range of temperatures. The densities were determined in a dilatometer constructed for the purpose, and the viscosities in a Fenske viscosimeter, modified to permit no air to come in contact with the sample at any time. The dilatometer was calibrated with methanol, which was also used as a reference liquid for the viscosity measurements. Methylhydrazine was found to have a density of 0.9433 gms/ml and an absolute viscosity of 13.319 centipoises at -52.0 °C; uns-dimethylhydrazine was found to have a density of 0.8684 gms/ml and an absolute viscosity of 5.114 centipoises at -55.0 °C. Data covering a range of temperatures are given in Tables I and II of the Appendix.

2. Comparative Tests of Methylhydrazine, Uns-Dimethylhydrazine and Hydrazine with Various Packing Materials

In order to find a safe packing material for the shipment of methylhydrazine and uns-dimethylhydrazine, experiments were per-

formed to determine the behavior of these compounds with various substances which could be used as an absorbent cushioning material. Tests with hydrazine were run in parallel for comparative purposes.

The tests were performed by placing in a beaker 50 mls of the packing material and then adding to it 10 mls of the hydrazine compound. A thermometer was inserted in the center of the beaker so that the bulb was covered by the mixture. The rise of temperature with elapsed time was noted as well as any other significant phenomena. Results are given in Tables III to IX in the Appendix.

As will be noted, these tests served also to compare the relative sensitivity of the three hydrazines to catalytic influences in the presence of air. The results show uns-dimethylhydrazine to be much less sensitive to these catalytic influences and therefore much safer to handle and to use than hydrazine or methylhydrazine.

In a number of cases hydrazine and methylhydrazine ignited spontaneously after a short interval of time, and in other cases temperature rises as high as 250°C or higher were noted. On the other hand, uns-dimethylhydrazine showed no sensitivity in most cases, and in the worst case showed a temperature rise to only 42°C after 56 minutes of contact time.

Similar tests performed with methylhydrazine and uns-dimethylhydrazine

in contact with glass blowing wool from which air had been displaced by nitrogen and with nitrogen atmosphere above showed no rise of temperature with time.

3. Ethylenehydrazine

In a previous technical report (Ref. 1) a method for the preparation of ethylenehydrazine by an adaptation of the Wenker method for the preparation of ethylenimine (Ref. 2) was described. This process results in a relatively low yield of product which is difficult to purify. An extractive method of purification was developed which yielded at that time a product of 91.5% purity.

Subsequently a special report (Ref. 3) described the preparation of ethylenehydrazine with a purity of 97.7% based on analysis with acid and with iodate. Since then a product close to 100% pure has been prepared. This material has a melting point of -40.5°C.

Because of the low yields of ethylenehydrazine obtained by the modified Wenker method, and the difficulties in purification, several other methods have been attempted.

The following reactions were described in Reference 1:

a. Reaction of ethylene bromide with hydrazine

b. Low-temperature nitrosation of ethylenimine, to be followed by reduction with lithium aluminum hydride.

c. Reaction of ethylenimine with hydroxylamine-O-sulfonic acid.

Other methods which have been attempted since then follow:

d. Further modifications of the Wenker Method:

(1) Reactions in which water-insoluble hydrocarbons, such as cumene, were added as diluents and heat transfer media, so that the reaction could be run with a minimum amount of water and with rapid removal of product. No improvement over original method was noted.

(2) Reactions using ethylene glycol as diluent and heat transfer medium. No improvement was noted.

(3) Reactions using tri-n-butylamine as a base instead of inorganic caustic. No product was obtained.

(4) A slurry of hydrazineoethylsulfate and caustic solution is dropped into the distilling flask which contains a small amount of hot caustic solution. Distillation of product proceeds as the hydrazinoethylsulfate slurry is added. The yield is about the same as that obtained by the original method, but this procedure is much more convenient, since it obviates foaming, is more easily controlled and requires less volume per unit of product.

e. Reaction of the toluenesulfonate ester of ethanolhydrazine with sodium hydroxide.

It was hoped that the toluenesulfonate ester of ethanolhydrazine might produce better results than does the sulfuric acid ester, which is employed in the Wenker process. First the toluenesul-

fonate salt of ethanolhydrazine was prepared as a crystalline compound and this substance was treated with further toluenesulfonic acid for preparation of the ester by thermal dehydration. Difficulties were encountered in this phase of the process, and it was not possible to obtain any pure substance identifiable as the ester. Impure products treated with caustic and heat did not appear to produce any ethylenehydrazine. However, the utility of this method cannot be ruled out as long as the required ester intermediate has not been obtained and identified.

f. Reactions with B-Chloroethylsulfate

Bis-B-chloroethylsulfate was prepared by the reaction of bis-B-chloroethylether with sulfur trioxide. Attempts were then made to alkylate hydrazine with this reagent in order to obtain a B-chloroethylhydrazine intermediate, or to obtain ethylenehydrazine directly in the presence of a sufficient quantity of caustic. As the result of a reaction in which no attempt was made to isolate the intermediate, a product was obtained which appeared to contain ethylenehydrazine in a greater state of purity than is obtained by the Wenker process, although the total yield of crude product was no greater. Examination of the product of this reaction is now in progress.

g. Reactions with B-chloroethyltoluenesulfonate

Just as with bis-B-chlorethylsulfate, the reagent, B-chloroethyl-toluenesulfonate, was used for the purpose of getting B-chloroethylhydrazine as an intermediate, or ethylenehydrazine as final product without isolation of intermediate. The initial stage of this reaction is similar to that of bis-B-chloroethylsulfate, but is slower and easier to control. Final products have not yet been examined, but the evidence at this stage is encouraging.

h. Modified Raschig Procedure

Reactions were performed which were analogous to the Raschig process for the manufacture of hydrazine. In this case the chloramine intermediate was reacted with ethylenimine. A product was obtained which is more volatile than hydrazine and is capable of reducing iodate. Evidently a hydrazine derivative is produced by this process. However, it has not yet been isolated or identified. This work is in progress.

4. N, N-dimethyl-N', N'-ethylenehydrazine

Some experiments directed toward the preparation of dimethyl-ethylenehydrazine were reported in Reference 1. At that time difficulty had been encountered in the preparation of the first intermediate, N-B-hydroxethyl-N', N'-dimethylhydrazine, by the reaction of ethylene oxide with uns-dimethylhydrazine. A procedure given

in the literature had been followed but little of the desired product could be obtained. A modification of this process was successful. The hot vapors of the uns-dimethylhydrazine were reacted with gaseous ethylene oxide in such manner that the resulting high boiling product condensed out at once and was removed from the reaction zone. This improved process can also be applied to the preparation of B-hydroxyethylhydrazine.

The N-B-hydroxyethyl-N', N'-dimethylhydrazine was treated with sulfuric acid in order to obtain, first, the sulfate salt, and finally the sulfate ester. No crystalline salt could be obtained, and to date no material identifiable as the ester. This work is continuing.

5. Production of Hydrazine Derivatives for Distribution To Various Agencies

As a result of the considerable interest in hydrazine derivatives which developed among various agencies, an addendum was incorporated in the present contract which called for the production and distribution of several hundred pounds of these derivatives.

Metalectro Corporation had developed a new process which made it possible to cope with this requirement in the short space of time allowed and with the relatively small budget for the purpose. By the application of this process it was possible

to bring the effort to a successful conclusion. The quantities of material manufactured and shipped under this contract requirement were 224 pounds of methylhydrazine and 140 pounds of unsymmetrical dimethylhydrazine. The compounds were prepared with a purity of 97% or better, the difference from 100% being primarily the homologous methylhydrazine derivative. In some cases the purities rose as high as 99% or better. Incidental to the development of new processes for the preparation of methyl derivatives of hydrazine, new processes for the preparation of trimethylhydrazine and tetramethylhydrazine as well as symmetrical dimethylhydrazine were found. Two pounds of symmetrical dimethylhydrazine were also shipped as part of the contract requirement.

CONFIDENTIAL

APPENDIX

TABLE I

DENSITIES AND VISCOSITIES OF METHYLHYDRAZINE

Temperature oC	Density gms/ml	Absolute Viscosity (centipoises)	Kinematic Viscosity (centistokes)
25.0	0.8743	0.781	0.893
0.0	0.8966	1.347	1.503
-30.0	0.9182	3.467	3.776
-37.0	0.0246	4.821	5.214
-45.0	0.0319	7.279	7.811
-50.3	0.0382	11.673	12.442
-52.0	0.9433	13.319	14.119

CONFIDENTIAL

APPENDIX

TABLE II

DENSITIES AND VISCOSITIES OF UNS-DIMETHYLHYDRAZINE

Temperature °C	Density gms/ml	Absolute Viscosity (centipoises)	Kinematic Viscosity (centistokes)
25.0	0.7861	0.509	0.647
13.8	0.7968	0.601	0.754
10.0	0.8017	0.645	0.805
0.0	0.8123	0.783	0.964
-5.0	0.8176	0.878	1.074
-15.0	0.8278	1.108	1.338
-25.0	0.8376	1.462	1.745
-35.0	0.8483	2.026	2.389
-45.0	0.8578	3.078	3.588
-55.0	0.8684	5.114	5.889

CONFIDENTIAL

CONFIDENTIAL

APPENDIX

TABLE III

SENSITIVITY TO CATALYTIC EFFECTS IN AIR

VERMICULITE

Temperature °C

Time, Minutes	Hydrazine	Methylhydrazine	Uns-Dimethylhydrazine
0	27	27	27
1	29	28	26.5
2	30	29	27
3	31	30	27
4	32.5	31	27
5	34	32	27
10	37	35.5	26
15	39	42	--
20	40.8	49.8	--
30	44	58.8	--
60	48	62	30
80	51	90	
94	55	108	
95	--	106	
98	--	97	
100	--	90	

Ten mls of the hydrazine compound were added to 50 mls of the vermiculite. None of the temperatures shown under uns-dimethylhydrazine were above ambient temperature.

TABLE IV

SENSITIVITY TO CATALYTIC EFFECTS IN AIR

ASBESTOS (INSULATING VARIETY)

Time, Minutes	Temperature °C		
	Hydrazine	Methylhydrazine	Uns-Dimethylhydrazine
0	31	29.5	30
1	33.5	33	30.5
2	37	34.5	30.5
3	39.5	--	--
7	Ignition at end of 3 min.	--	29.5
8		46	--
		Ignition at end of 8 minutes. Flame was smothered and thermometer replaced.	
25	--	122	--
30	--	140	--
31	--	155	--
32	--	167	--
33	--	176	--
34	--	187	--
35	--	220	30

Ten mls of the hydrazine compound were added to 50 mls of the asbestos. None of the temperatures shown under uns-dimethylhydrazine were above ambient temperature.

CONFIDENTIAL
APPENDIX

TABLE V

SENSITIVITY TO CATALYTIC EFFECTS IN AIR

ASBESTOS (ACID WASHED)

Time, Minutes	Temperature °C		
	Hydrazine	Methylhydrazine	Uns-Dimethylhydrazine
0	32	32	33
1	39	35	33
2	47	36	33
3	54	40	33
5	62	48	33
10	74	64.2	35
15	--	73	--
17	--	81	--
18	--	110	--
19	--	159	--
20	82	230	37
21 to 23	--	>250	--
24	--	210	--
25	--	190	--
30	88	100	38
40	93	52	38
50	96	--	39
52	151	--	--
54	206	--	--
56	261	--	42

Ten mls of the hydrazine compound were added to 50 mls of the asbestos.

CONFIDENTIAL

APPENDIX

TABLE VI

SENSITIVITY TO CATALYTIC EFFECTS IN AIR

MAGNESIA (85% MAGNESIA - 15% ASBESTOS)

Time, Minutes	Temperature °C		
	Hydrazine	Methylhydrazine	Uns-Dimethylhydrazine
0	32	31	31
1	32.5	32	29
2	34	33	28
3	35	40	27.5
5	--	47	27
7	--	53	27
8	--	58 Ignition after 8 minutes	27
10	41.5		--
15	42.2		--
20	41		--
25	39 Ignition after 25 minutes		27

Ten mls of the hydrazine compound were added to 50 mls of the magnesia. None of the temperatures shown under uns-dimethylhydrazine were above ambient temperature.

CONFIDENTIAL
APPENDIX

TABLE VII

SENSITIVITY TO CATALYTIC EFFECTS IN AIR

ASBESTOS (LOW IRON)

Time, Minutes	Temperature °C		
	Hydrazine	Methylhydrazine	Uns-Dimethylhydrazine
0	32	31	31
2	37	36	--
5	51	49.5	32
8	60	--	--
	Ignition after 8 minutes		
10	--	68	35
13	--	76	--
		Ignition after 13 minutes	
15	--	--	40
20	--	--	36

Ten mls of the hydrazine compound were added to 50 mls of the asbestos.

CONFIDENTIAL
APPENDIX

TABLE VIII

SENSITIVITY TO CATALYTIC EFFECTS IN AIR

GLASS WOOL (INSULATION GRADE)

Temperature °C

Time, Minutes	Hydrazine	Methylhydrazine	Uns-Dimethylhydrazine
0	28	28	28
5	29	32	24
10	30	35	24
15	31	38	24
20	34	43	24
25	35	49	24
30	36	55	25
40	38	74	26
45	38	79	26

Ten mls of the hydrazine compound were added to 50 mls of the glass wool. None of the temperatures shown under uns-dimethylhydrazine were above ambient temperature.

CONFIDENTIAL

APPENDIX

TABLE IX

SENSITIVITY TO CATALYTIC EFFECTS IN AIR

Comparison of Pyrex Glass Wool (Laboratory Grade) vs. Glass Wool (Insulation Grade) using only Methylhydrazine

Time, Minutes	Temperature °C	
	Pyrex Glass Wool	Glass Blowing Wool
0	26	26
5	30	29.5
10	46	34.5
20	62	48
30	71	76
35	71	83
40	72	79
50	73	69
55	71	58
60	69	53.5

Ten mls quantities of methylhydrazine were added to 50 ml volumes of the respective glass wool samples.

REFERENCES

1. Metalectro Corporation, Technical Report No. M-52-1-ONR, March 1, 1953, "Improved Liquid Propellants: Systems with Hydrazine; Hydrazine Derivatives." (Confidential)

2. Wenker, H., Jour. Amer. Chem. Soc. 57, 2328 (1935).

3. Metalectro Corporation, Communication to Chief of Naval Research, Office of Naval Research, Attention: Head, Power Branch, April 3, 1953. (Confidential)

UNCLASSIFIED